



Kinetic behaviour of HC-SCR over Ag/alumina catalyst using a model paraffinic second generation biodiesel compound

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ABSTRACT

The effect of longer paraffins on the mechanism of the HC-SCR reaction over a 1.91 wt.% Ag/alumina catalyst was investigated by kinetic studies. Hexadecane (C₁₆H₃₄) was chosen as a model compound as it is also a representative molecule for a second generation biodiesel consisting of only long-chain paraffins. The kinetic behaviour of the catalytic reduction of NO_x was examined at steady-state conditions in the temperature range 250–550 °C (50 °C ramping) and by using the following gas concentrations: P_{NO} = 100, 250, 500, 750 or 1000 ppm, P_{hexadecane} = 31, 94, 188, 281 or 375 ppm and P_{O₂} = 1.5, 3, 4.5, 6 or 9 vol.%. Results showed that in the temperature range 250–425 °C high hexadecane concentration had an inhibiting effect on the NO reduction. At temperatures above 350 °C the apparent reaction orders for hexadecane with respect to hexadecane increased to close or above 1. Reaction orders towards NO were close to 0.55 indicating that NO adsorption on the catalyst surface is stronger than hexadecane adsorption. Based on the experimental data it is proposed that small clusters alone cannot be the active sites for HC-SCR over Ag/Al₂O₃ but the important requirement for high activity over the catalyst is the local concentrations of hydrocarbon and NO on the interface of silver and the support.

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1. Introduction

The development of catalytic materials to reduce nitrogen oxides (NO_x) under excess oxygen has been intensive during the past decades and several catalytic techniques, such as selective catalytic reduction with ammonia or hydrocarbons (NH₃-SCR, HC-SCR) and NO_x-storage have shown promising results [1–5]. However, none of these techniques can yet provide a fully satisfactory package to meet the new strict emission standards for NO_x reduction from diesel vehicles. Especially reduction activity at low temperatures (below 250 °C) and in fast transient conditions, resistance against catalyst deactivation and cost effectiveness need to be improved.

Among the different NO_x reduction techniques developed for automotive applications selective catalytic reduction with hydrocarbons (HC-SCR) offers a very simple solution compared to other techniques. Since the early work of Iwamoto [1] and Held [2] on the hydrocarbon selective catalytic reduction, several catalytic formulations have been suggested [6–27]. Among the tested materials, silver supported on alumina (Ag/Al₂O₃) has been reported as one of the most promising candidate. Moreover, it has been proven in laboratory, engine bench and full-scale vehicle

tests with model compounds and special (MK1) diesel fuels to be a very active catalyst [8,9,12,17]. However, the high activity is mainly connected to the use of model compounds or extra pure commercial diesel and elevated temperatures (>300 °C). Especially the requirements of high temperature represent a severe drawback for the system to be used in combination with modern diesel engines having exhaust gas temperature of 200 °C or less for most of the time during the NEDC test [9].

An additional challenge for HC-SCR system is the gradual increase in the use of bio-based fuels, since especially over the silver system the reduction activity is strongly connected to the nature of the reducing agent [11–15,21,22]. Fuels derived from triglycerides can be used as substitutes for fossil based diesel fuels directly and thus fatty acid methyl and ethyl esters derived via transesterification of triglycerides have attracted most attention [23]. In addition, the catalyst activity in HC-SCR is related to the sulphur and aromatic content of the fuel, poisoning or blocking the active sites. Thus, biofuels may here offer a solution to improved low temperature HC-SCR activity, as they do not contain sulphur or aromatics.

In this paper a kinetic study of C₁₆H₃₄-SCR of NO_x over Ag/Al₂O₃ catalyst under lean conditions is presented. Emphasis has been put on experiments with simulated diesel exhaust mixtures, where the concentrations of the reactants (NO, C₁₆H₃₄ and O₂) are varied at steady-state conditions. Based on the experimental results the kinetic behaviour for NO reduction and hydrocarbon oxidation at

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different temperature and concentration regions as well as apparent reaction orders are reported in this paper. In addition, the kinetic behaviour of $C_{16}H_{34}$ -SCR is compared to our previous work with C_8H_{18} -SCR [26] and an explanation for the different behaviour between the two compounds is proposed. Hexadecane is also an interesting substance as it can be considered as a representative model compound for the fully formulated second generation biodiesel produced by the Finnish oil company Neste Oil. In this process, called NextBTL, high quality biodiesel consisting of only higher paraffins, mainly in the C_{15} – C_{18} range, are produced. Traditionally commercial diesel fuel is not preferred in mechanistic studies due to its complex composition including impurities which might lead to incorrect interpretation of the results, especially concerning the reaction mechanism. However, biodiesel produced with the NextBTL process is already in test use in the local traffic in the capital city region of Finland and moreover it is used, after hydrotreating and isomerisation of bio-based oils as such, not only as a blend. Thus the results from the laboratory studies with hexadecane are of high relevance and can be used for catalyst development per se. Moreover, the known composition of the used fuel (NextBTL biodiesel) could offer possibilities for precise and optimized hydrocarbon feeding system in the exhaust aftertreatment system of a vehicle.

In addition, the relevance of kinetic models in the case of HC-SCR is discussed. For catalytic processes, where the knowledge of reaction mechanism and active catalytic sites is limited, the development of a kinetic model can be challenging. This is rather because of the very complex reaction mechanism of HC-SCR where the activity depends on the nature, spatial arrangement and functional groups of the reducing agent, but not a consequence of insufficient experimental work. Therefore, creating a proper kinetic model is a very difficult task for HC-SCR over Ag/Al_2O_3 but at the same time a global model able to predict the catalytic performance under the operational conditions is of great importance.

2. Experimental

The catalyst used in this study was a 1.91 wt.% Ag /alumina catalyst prepared by impregnation of a commercial alumina support (LaRoche Industries Inc.) with a 0.022 M silver nitrate solution followed by drying and calcination, resulting in a B.E.T. surface area of approximately $190\text{ m}^2/\text{g}$ of the final catalyst [20]. The crushed and sieved Ag /alumina (0.2 g, 250–500 μm) catalyst was tested in a fixed bed quartz reactor inserted in an oven equipped with a temperature controller. Special experiments according to [26] were carried out to ensure that the kinetics is measured in the absence of external and internal diffusion limitations. A temperature range of 250–550 °C with 50 °C ramping and sampling at steady-state conditions with GHSV = 60,000 or 120,000 h^{-1} (residence time 0.034 or 0.017 s) and total flow rate of 550 ml/min were applied for the catalytic activity tests.

To determine the effect of NO , $C_{16}H_{34}$ and O_2 concentrations on the NO to N_2 and $C_{16}H_{34}$ to $CO + CO_2$ conversions, the experiments were carried out by varying the concentration of one reactant at a time in the feed gas mixture while the concentrations of others were kept constant. The following concentrations were used: 100, 250, 500, 750 and 1000 ppm NO , 31, 94, 187, 281 and 375 ppm hexadecane, 1.5, 3, 4.5, 6 and 9 vol.% O_2 and He as a balance. The used hydrocarbon concentrations correspond to HC_1/NO ratios equal to 1, 3, 6, 9 and 12. The concentration of H_2O was kept constant at 12 vol.% in all tests using a syringe pump (IVAC P6000 Medical Systems) combined to a controlled evaporator mixer (Bronkhorst HI-TEC). All the gases were of high purity (AGA) and were introduced into the reactor by means of mass flow-controllers (Brooks 5850). The addition of hexadecane took place

via a syringe pump (CMA 102/Microdialysis). Oxygen was fed separately into the reactor to avoid oxidation of NO before the catalyst bed. The effluent gas (both NO to N_2 and hexadecane to $CO + CO_2$) was analyzed by a GC (HP 6890 series) equipped with a GS Q column, a GS Molesieve column (J&W Scientific) and FI as well as TC detectors. High purity calibration gases (AGA) were used for calibration of the NO_x analyser and the gas chromatograph.

The acidity of the catalyst was measured by infrared spectroscopy (ATI Mattson FTIR) by using pyridine ($\geq 99.5\%$, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The catalyst was pressed into a thin self-supported wafer. Pyridine was first adsorbed for 30 min at 100 °C and then desorbed by evacuation at different temperatures (250, 350 and 450 °C) with subsequent measurements to obtain a distribution of acid site strengths. All spectra were recorded at 100 °C with a spectral resolution of 2 cm^{-1} . Spectral bands at 1545 and 1450 cm^{-1} , respectively, were used to identify Brønsted and Lewis acid sites. The amounts of acid sites were calculated from the intensities of corresponding spectral bands by using molar extinction coefficients reported by Emeis [28].

3. Results and discussion

3.1. Results from activity tests

The NO to N_2 conversion in $C_{16}H_{34}$ -SCR over a 1.91 wt.% Ag /alumina catalyst as a function of temperature is shown in Fig. 1 using GHSV = 60,000 h^{-1} . Previously [26] it has been demonstrated that NO reduction over a similar catalyst was optimized at HC_1/NO ratio equal to 6 when octane was used as the reducing agent. Therefore, the same ratio was chosen for the first screening of the catalytic activity with hexadecane. Moreover, for C_8H_{18} -SCR it has been shown that a clear beneficial effect on the NO reduction is achieved by increasing the hydrocarbon concentration until a saturation point was reached [26]. As the activities in C_8H_{18} - and $C_{16}H_{34}$ -SCR are compared (Fig. 1) it can be seen that the reduction activity in the temperature range 150–350 °C is considerably higher with hexadecane as a reducing agent. However, above 350 °C the situation is quite the opposite; in octane-SCR the conversion of NO to N_2 continues to increase until reaching the maximum, approximately 95%, at 450 °C. Thereafter, the reduction activity slightly decreases along with the increasing temperature, which is due to competing total oxidation of octane leading to the lack of sufficient amount of reducing agent for SCR reaction.

As the high temperature (350–600 °C) NO conversion in $C_{16}H_{34}$ -SCR only reaches roughly half of that in C_8H_{18} -SCR the result clearly deviates of those earlier reported for HC-SCR over Ag /

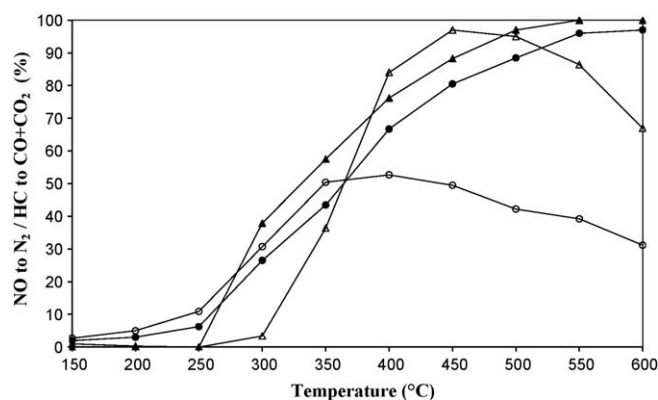


Fig. 1. NO to N_2 (Δ , \circ) and hydrocarbon to $CO + CO_2$ (\blacktriangle , \bullet) conversion over a 1.91 Ag/Al_2O_3 catalyst with 375 ppm n - C_8H_{18} (Δ , \blacktriangle) or 188 ppm n - $C_{16}H_{34}$ (\circ , \bullet), $HC_1/NO = 6$ in both cases. Gas flow: 500 ppm NO , 375 ppm n - C_8H_{18} or 188 ppm n - $C_{16}H_{34}$, 6 vol.% O_2 , 12 vol.% H_2O and He balance, GHSV = 60,000 h^{-1} .

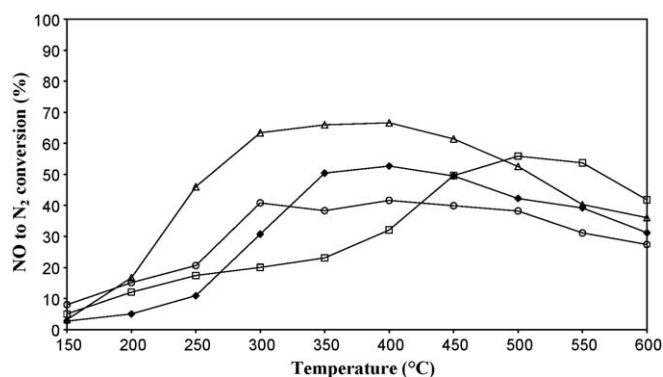


Fig. 2. NO to N₂ conversion over a 1.91 Ag/Al₂O₃ catalyst using 94 ppm (○), 188 ppm (◆), 375 ppm n-C₁₆H₃₄ (□) or 188 ppm + 1 vol.% H₂ (△). Gas flow: 500 ppm NO, 94, 188 or 375 ppm ppm n-C₁₆H₃₄, 6 vol.% O₂, 10 vol.% CO₂, 350 ppm CO, 0 or 1 vol.% H₂ and 12 vol.% H₂O and He balance. GHSV = 60,000 h⁻¹.

alumina with paraffins having lower chain length, e.g. with propane, octane or decane [22,26,29]. They all result in a NO to N₂ conversion close to or over 90% at comparable space velocities.

For SCR reaction over silver catalysts simultaneous oxidation of the reducing agent and reduction of NO occur and the activity of the catalyst is bound to its capability to activate through partial oxidation of the reducing agent [26,30,31]. Thus the difference in activities between C₈H₁₈- and C₁₆H₃₄-SCR could be explained if the observed oxidation behaviour would differ in the same manner as the reduction activities. However, as shown in Fig. 1 the observed oxidation curves for both hydrocarbons are almost identical. This intriguing behaviour will be discussed later in the paper.

After the experiment at HC₁/NO = 6 the hexadecane concentration was decreased to correspond HC₁/NO = 3. As it can be seen (Fig. 2) the NO reduction resulted in clearly higher conversion values in the temperature range 150–325 °C compared to HC₁/NO = 6 and higher conversion values in the temperature range 150–425 compared to HC₁/NO = 12. Based on the results shown in Fig. 2 it can be concluded that the SCR reaction was mostly enhanced by decreasing the partial pressure of the reducing agent in the domain close to or below the boiling point of hexadecane (i.e. 287 °C). A possible reason for such different behaviour compared to octane [26] in this temperature range can be the larger heat of adsorption of hexadecane [32,33]. The stronger adsorption combined to C₁₆H₃₄ larger physical size might lead to the larger occupation of silver surface thus limiting the adsorption of other components resulting in decreased reduction activity. It cannot either be totally excluded that hexadecane is condensed on the surface and for the SCR reaction to take place diffusion of gas phase (NO and O₂) reactants through the liquid film is needed. If condensation of the reducing agent takes place on the catalyst surface then the reaction rate obviously decreases compared to two-phase (gas-surface) reactions.

When the concentration of hexadecane was doubled to correspond HC₁/NO = 12 the observed NO to N₂ conversion clearly increased in the temperature range 425–600 °C compared to that recorded at the HC₁/NO = 3 or 6 (Fig. 2). Such behaviour can be explained by the fact that due to increased total oxidation of the hydrocarbon, which competes with the SCR reaction at high temperatures, more reducing agent simply needs to be introduced in the system.

Finally, the effect of 1 vol.% hydrogen on the NO to N₂ reduction with hexadecane, keeping the HC₁/NO ratio constant at 6, was studied (Fig. 2). As it can be seen, the reduction activity clearly increased in the temperature range 200–500 °C as hydrogen was added to the gas mixture. Previously [31] it has been demonstrated that hydrogen alone does not reduce NO over Ag/alumina catalyst under lean conditions and that the positive effect of adding hydrogen in the gas feed is prominent mainly in the low

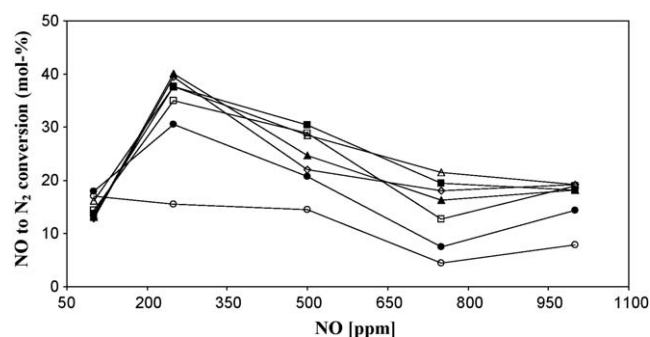


Fig. 3. Effect of NO concentration on NO to N₂ reduction over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 350 °C (□), 400 °C (■), 450 °C (△), 500 °C (▲) and at 550 °C (◇). Gas flow: 100, 250, 500, 750 or 1000 ppm NO, 188 ppm C₁₆H₃₄, 6 vol.% O₂, 12 vol.% H₂O and He as balance. GHSV = 120,000 h⁻¹.

temperature region [17,18,34–36]. The increased activity at high temperature range compared to that in octane-SCR indicates that the underlying mechanistic explanation is somewhat different for C₁₆H₃₄-SCR or that the beneficial effect of hydrogen in C₈H₁₈-SCR cannot be detected at high temperature range due to very high reduction rate. A tentative explanation for such experimental behaviour would be that due to different reactivity of the alkanes (C₈ vs. C₁₆) the formation of certain intermediate(s), crucial for high temperature NO reduction over Ag/alumina, is not sufficient in C₁₆H₃₄-SCR and thus the activity above 350 °C is suppressed compared to the activity in C₈H₁₈-SCR. Then by adding hydrogen the reaction rate of certain key elementary steps involved in the reaction mechanism is enhanced or new reaction routes are created in a way that the formation of the crucial intermediate(s) increase(s) as well as increases the NO reduction activity when higher (more reactive) alkanes are used as reducing agents.

3.2. Varying NO concentration

The effect of varying NO concentration (100–1000 ppm) on the NO to N₂ reduction activity and reduction rates over the silver catalyst is shown in Figs. 3 and 4 and on the hexadecane oxidation in Fig. 5. As it can be seen the NO conversion goes through the maximum at NO = 250 ppm and the highest reduction activity was recorded at the two highest temperatures, i.e. at 500 and 550 °C (Fig. 3) when HC₁/NO ratio was fixed to 12. Houel et al. [37] demonstrated the same behaviour for HC-SCR over Ag/alumina when US06 diesel fuel was used as the reducing agent. Analyzing the results presented in Figs. 1 and 6, where the effect of C₁₆H₃₄ on the NO conversion was studied either by keeping the ratio constant

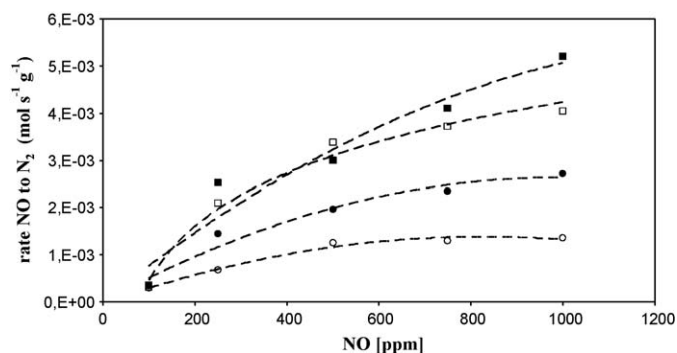


Fig. 4. NO to N₂ reduction rate versus NO concentration over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 400 °C (□) and 550 °C (■). Gas flow: 100, 250, 500, 750 or 1000 ppm NO, 188 ppm C₁₆H₃₄, 6 vol.% O₂, 12 vol.% H₂O and He as balance. GHSV = 120,000 h⁻¹.

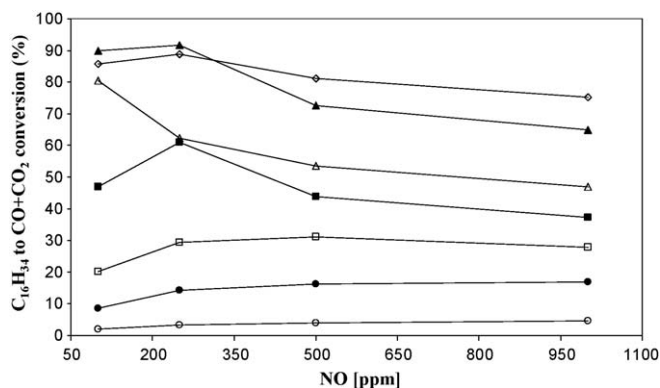


Fig. 5. Effect of NO concentration on C₁₆H₃₄ to CO + CO₂ oxidation over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 350 °C (□), 400 °C (■), 450 °C (△), 500 °C (▲) and at 550 °C (◇). Gas flow: 100, 250, 500 or 1000 ppm NO, 188 ppm C₁₆H₃₄, 6 vol.% O₂, 12 vol.% H₂O and He as balance. GHSV = 120,000 h⁻¹.

at 6 (Fig. 1) or by changing the HC₁/NO ratio between 1 and 12 (Fig. 6) it can be concluded that with higher hydrocarbons the effect of the competing total oxidation can be counteracted by increasing the hydrocarbon concentration in the gas mixture. Thus the highest reduction activity was recorded at the highest temperature and at the highest HC₁/NO ratio. In Ref. [26] the effect of increasing the HC₁/NO ratio from 6 to 8 in C₈H₁₈-SCR did not result in increased NO reduction activity at 500 and 550 °C, however it should be noted that the overall conversion was much higher than in C₁₆H₃₄-SCR.

As the NO concentration was further increased to 500 or 750 ppm (HC₁/NO = 6 or 4), the overall conversion decreased at all temperatures as expected. The main difference observed along with the increasing NO concentration was, that the highest NO conversion was recorded at lower temperatures, namely between 350 and 450 °C. Above 450 °C the NO to N₂ reduction activity clearly decreased, which can be attributed to the competing total oxidation of the reductant as the HC₁/NO ratio decreased to 6 and 4, respectively. At the highest NO concentration (1000 ppm) the reduction activity was further decreased and the difference between activities above 300 °C was not as clear as at lower NO concentrations. The experimental results confirm and support the observation made above that the NO reduction is limited by the hydrocarbon concentration at high temperatures whereas at lower temperatures, i.e. 250–300 °C, the thermal stability of nitrate species could be rate limiting [7,27]. As the NO concentration was further increased a clear decrease in the reduction activity was observed confirming an apparent inhibiting effect of NO concentration on the NO reduction rate. However, when the actual reduction rates were plotted against

Table 1

Reaction orders of NO and hexadecane at different temperatures.

Temperature (°C)	Order C ₁₆ H ₃₄ in C ₁₆ H ₃₄ oxidation	Order NO in NO reduction
250	0	0.67
300	0	0.56
350	0.54	0.90
400	1.06	0.61
450	1.09	0.65
500	1.15	0.52
550	1.23	0.62

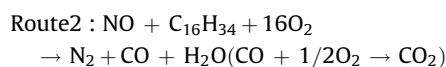
the NO concentration (Fig. 4), it was found that the rates were very low at low NO concentrations, i.e. 100–250 ppm, at all temperatures but increased along with the increasing NO concentration until approaching zero order kinetics at high NO concentrations.

The apparent reaction orders for NO reduction with respect to NO are shown in Table 1. As it can be seen, all the orders vary between 0.5 and 0.6 except those recorded at 350 °C, which should thus be taken with caution. On the other hand, 350 °C is the temperature where the maximum NO conversion is reached indicating a change on the NO surface coverage. The other measured reaction orders indicate relatively high but constant NO coverage and that the NO reduction is rather strongly dependent on the NO concentration. However, compared for instance to the NO orders reported for propane-SCR [29] the inhibiting effect NO is clearly not so dominating and could be connected to the stronger adsorption or greater reactivity of hexadecane. Moreover, compared to our previous results with octane [26], where we recorded zero order kinetics for NO at temperatures below 550 °C, the orders of NO are clearly higher in C₁₆H₃₄-SCR indicating lower NO coverage in hexadecane- than in propane- and octane-SCR. The apparent activation energies for NO reduction at different NO concentrations were also calculated and were approximately 25 kJ/mol. However, due to the complex nature of the reaction mechanism the results should be viewed as indicative. It can be mentioned that in the temperature range 400–550 °C the apparent activation energies were not strongly affected by the NO concentration.

The effect of NO concentration on the hexadecane to CO + CO₂ conversion is shown in Fig. 5. As it can be seen, NO has only a minor dependence on the C₁₆H₃₄ oxidation activity and also on the actual rates (not shown), but the overall activity increases rapidly along with the increasing temperature indicating total oxidation. In addition, as the recorded NO reduction rates at low NO concentration (Fig. 4) were very low, it is proposed that the major reaction route in the NO concentration range 100–250 ppm is hydrocarbon oxidation with oxygen as a function of temperature. The calculated reaction orders also indicate higher oxygen and hexadecane surface coverage compared to NO coverage at these conditions. Thus the oxidation of hexadecane at low NO concentration is expected to occur along the reaction route 1 presented below:



On the other hand, as the NO concentration and thus the surface coverage increases, the reduction rates also increase (Fig. 4), whereas the hydrocarbon oxidation rates remain constant. As the HC-SCR reaction must obviously depend on the NO and hexadecane concentrations, thus a consequent explanation for the hydrocarbon oxidation at intermediate NO concentrations, i.e. 250–750 ppm, is the reaction with NO to finally produce N₂ and it can be described with a reaction route 2.



In both cases it is assumed that CO₂ is formed from CO. As the oxygen concentration was kept constant throughout the experi-

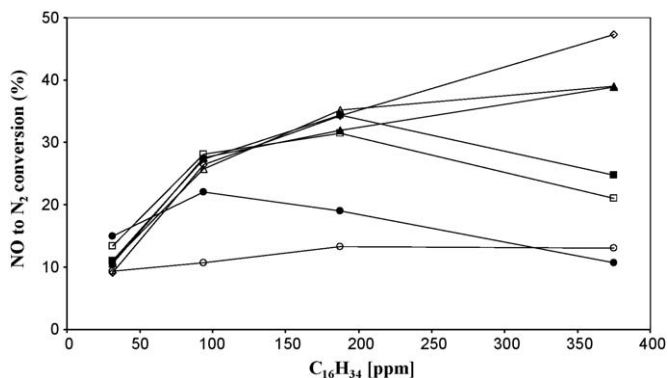


Fig. 6. Effect of C₁₆H₃₄ concentration on NO to N₂ reduction over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 350 °C (□), 400 °C (■), 450 °C (△), 500 °C (▲) and at 550 °C (◇). Gas flow: 31, 94, 188 or 375 ppm C₁₆H₃₄, 500 ppm NO, 6 vol.% O₂, 12 vol.% H₂O and He as balance. GHSV = 120,000 h⁻¹.

ments, the hydrocarbon oxidation should thus depend on the NO concentration as follows:

NO concentration 100–250 ppm → predominantly route 1

NO concentration 250–750 ppm → predominantly route 2

Furthermore, when the NO concentration increases above 750 ppm, the NO reduction rates approach zero order indicating a high NO surface coverage possibly starting to block the surface from adsorption of other species needed for the SCR reaction (Fig. 4). Interestingly, at the same time the effect of NO concentration on hexadecane conversion and on the oxidation rates remains low or negligible, which will be discussed in the next chapter. Based on the experimental results so far we can conclude the $C_{16}H_{34}$ -SCR at high NO concentrations as follows:

NO concentration 750–1000 ppm

→ route 1 is predominant compared to route 2

(+inhibition due to high NO surface coverage).

As mentioned above, the effect of NO concentration on the hexadecane oxidation rates was interestingly found to be almost non-existing. Such result indicates that the adsorption and reaction between oxygen and hexadecane is not possibly affected by the nitrogen oxide. Furthermore, it can be speculated that the hydrocarbon-oxygen reactions take place also on sites different from those on which the actual SCR reaction proceed. Thus the oxidation of the hydrocarbon can continue even if the NO coverage on the surface increases greatly. Then the formed oxygenates react with the active form of adsorbed NO.

3.3. Varying hexadecane concentration

The experimental results of the effect of the hexadecane concentration on the NO to N_2 conversion are shown in Fig. 6 and on the reduction rates in Fig. 7. As it can be seen, at 250 °C the effect of hydrocarbon concentration on the NO reduction activity is almost non-existing, which is in complete agreement with the activity test results. The reason that the NO reduction over the catalyst does not respond to the hydrocarbon concentration at low temperature is connected to the insufficient hydrocarbon activation (partial oxidation) leading to oxygenates needed for the SCR reaction to take place at low temperature. This can also be seen from Fig. 8. As the temperature was increased to 300–400 °C a clear positive response on the NO reduction rates is seen along with the increasing hydrocarbon concentration from 31 to 94 ppm. However, by further increasing the hydrocarbon concentration (94–375 ppm) a clear inhibiting effect on the NO to N_2 reduction was

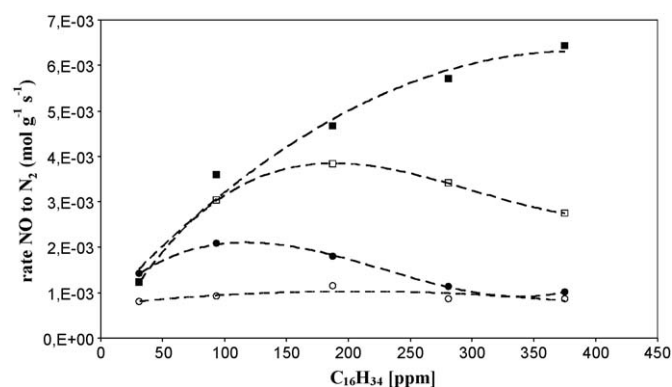


Fig. 7. NO to N_2 reduction rate versus $C_{16}H_{34}$ concentration over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 400 °C (□) and 550 °C (■). Gas flow: 31, 94, 188 or 375 ppm $C_{16}H_{34}$, 500 ppm NO, 6 vol.% O_2 , 12 vol.% H_2O and He as balance. GHSV = 120,000 h^{-1} .

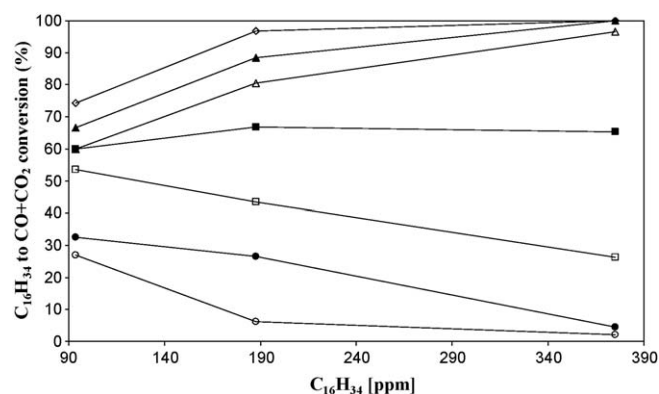


Fig. 8. Effect of $C_{16}H_{34}$ concentration on $C_{16}H_{34}$ to CO + CO_2 oxidation over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 350 °C (□), 400 °C (■), 450 °C (△), 500 °C (▲) and at 550 °C (◇). Gas flow: 94, 188 or 375 ppm $C_{16}H_{34}$, 500 ppm NO, 6 vol.% O_2 , 12 vol.% H_2O and He as balance. GHSV = 120,000 h^{-1} .

observed. Such behaviour is interesting, as in our previous study with octane [26] the increase of reductant concentration had only a positive effect on the reduction rates at comparable C_1 -concentrations in this temperature domain. As the surface coverage of hexadecane increases there are two possibilities. Either increasing the hexadecane concentration will inhibit the nitrogen oxide adsorption and thus the deNO_x reaction or it inhibits the oxygen adsorption thus the hydrocarbon oxidation is limited. However, from Fig. 9 it can be seen that increasing hexadecane concentration has a clear positive effect on the oxidation rates at the same temperatures where NO reduction rates are decreased due to increasing hexadecane concentration, i.e. at 300 and 400 °C. Considering this, hexadecane probably does not limit oxygen coverage on the surface. On the other hand, as the size of hexadecane, compared to octane, is twice as big, a possible explanation is that at high hexadecane concentrations the adsorption of nitrogen oxide is inhibited resulting in such a strong decrease in reduction rates as shown in Fig. 7. Thus, based on this it can be concluded as follows:

$C_{16}H_{34}$ concentration > 100 ppm → predominantly route 1 at 300 °C

and

$C_{16}H_{34}$ concentration > 180 ppm → predominantly route 1 at 400 °C

At higher temperatures, i.e. above 400 °C, a clear positive effect of the increasing hexadecane concentration was observed (Figs. 6 and 7). This means that the hexadecane coverage does not anymore inhibit the SCR reaction because the oxidation rate is so

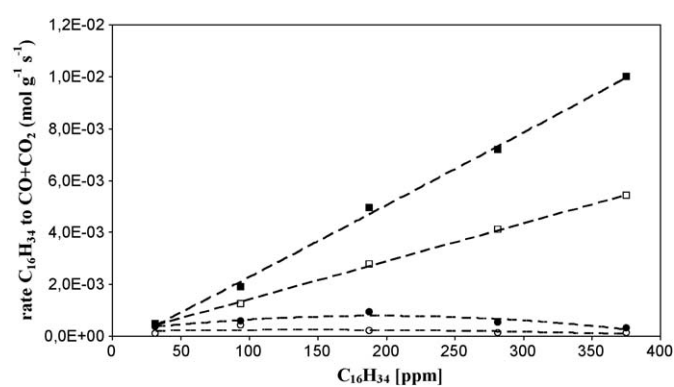


Fig. 9. Effect of $C_{16}H_{34}$ concentration on $C_{16}H_{34}$ to CO + CO_2 oxidation rate over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 400 °C (□) and 550 °C (■). Gas flow: 31, 94, 188 or 375 ppm $C_{16}H_{34}$, 500 ppm NO, 6 vol.% O_2 , 12 vol.% H_2O and He as balance. GHSV = 120,000 h^{-1} .

high. On the contrary, at high temperature domain the increased hexadecane concentration helps to counteract the unwanted total oxidation of the reductant resulting in increased SCR activity over the catalyst. Interestingly, in our previous study with octane such beneficial effect of increasing reductant concentration was not observed even if the SCR reaction was also found to clearly retard due to the competing total oxidation at high temperatures, i.e. above 500 °C.

Fig. 8 shows the effect of hexadecane concentration on the hexadecane oxidation. As it can be seen, in the temperature range 250–350 °C the effect of hexadecane concentration on its oxidation is almost negligible and the calculated empirical reaction orders were close to zero. When the hexadecane oxidation rates were plotted versus the concentration (Fig. 9) zero order kinetics was manifested in the temperature domain 250–350 °C. As the temperatures increased above 350 °C the dependence of hexadecane oxidation on its concentration turns to positive resulting in empirical reaction orders between 1 and 1.23 (Table 1) and the oxidation activity is approximately twofold the activity of NO reduction (Fig. 6). The high reaction orders indicate low hexadecane coverage on the surface.

The results of the activity tests of $C_{16}H_{34}$ -SCR (Fig. 2) clearly deviate from those recorded when octane (C_8) was used as the reducing agent [26]. Increasing hexadecane concentration ($HC_1/NO = 3 \rightarrow 12$) decreases the NO reduction activity in the temperature range 250–325 °C. Above 325 °C the lowest hexadecane concentration does not anymore result in the highest NO to N_2 conversion but the intermediate ratio ($HC_1/NO = 6$) shows clearly higher activity towards NO reduction between 325 and 600 °C. Furthermore, as the temperature rises above 425 °C, a clear beneficial effect of increasing hexadecane concentration ($HC_1/NO = 6 \rightarrow 12$), resulting in the reaction orders close or above one (Table 1), was observed. The recorded high reaction orders indicate low hexadecane coverage at these temperatures and that $C_{16}H_{34}$ activation is an important and kinetically significant step in the NO reduction. In addition, as already mentioned above, at higher temperatures the SCR reaction (route 2) benefits from the higher hydrocarbon concentration as the parallel competing total oxidation (route 1) would otherwise limit the reduction reaction.

At lower temperature the difference in activities at different hexadecane concentrations cannot be explained with the same rate determining step as at high temperatures. At the low temperatures the activation (partial oxidation) of the reducing agent is one of the rate limiting steps and is clearly dependent on the hydrocarbon concentration as follows from Fig. 2. Based on the experimental results reported in several studies [12,15,26,29,34] it can be stated that the reduction activity in HC-SCR over silver catalyst also strongly depends on the chain length of the hydrocarbon when paraffins are used as reducing agents. Houel et al. [37] have proposed that the underlying cause for decreasing activity at low temperatures using long-chain hydrocarbons (dodecane) or commercial diesel fuel (US06) and high HC_1/NO ratios is coking of the Ag/Al_2O_3 catalyst. In our ongoing study, where we investigated the deactivation of the Ag/Al_2O_3 catalyst (activity vs. time) using either a long-chained paraffin ($C_{16}H_{34}$) or commercial diesel (Finnish standard quality) fuel as reducing agents, a similar decrease in activity during the first 30 min was also observed in the beginning of the experiment at 250 °C. After the first 30 min the activity over the catalyst was, however, stabilised (Fig. 10). Coke is rather difficult to define, but it has been shown that its formation can take place at low temperatures [38] and from the liquid phase containing hydrocarbons [39], even if it is commonly connected to long contact time, strong acidity and capillary forces. Thus, a quantitative and qualitative analysis of the surface deposit was made. The results from GC–MS revealed that there is carbonaceous deposit on the catalyst surface after the

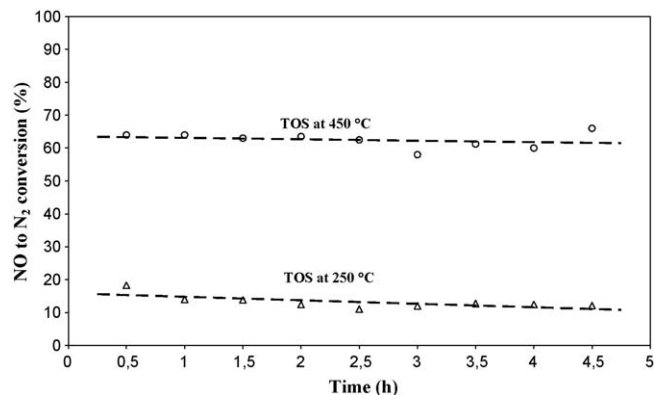


Fig. 10. Time-on-stream behaviour over the Ag/alumina catalysts at 250 °C (Δ) and 450 °C (○). Gas flow: 500 ppm NO, 188 ppm $n-C_{16}H_{34}$, 6 vol.% O_2 , 10 vol.% CO_2 , 350 ppm CO, 12 vol.% H_2O and He balance. GHSV = 60,000 h^{-1} .

experiment at 250 °C present as paraffins and olefins in the C_{12} – C_{19} range. Therefore, it can be concluded that even if the aluminum oxide used in the present study is a mesoporous material and does not have strong Brønsted acid sites but contains only a small amount of Lewis acid sites (Table 2), carbonaceous species are formed on the surface at low temperature and at high HC_1/NO ratios when long-chained paraffins or commercial diesel are used. However, based on the current data it cannot be concluded whether the declined activity in the beginning of the experiment depends on blocking of the active sites by the carbonaceous species deposited on the surface. Based on the GC–MS analysis the deposits have much longer chain lengths than octane resulting in higher heat of adsorption and moreover, is close to the length of hexadecane. Thus, another explanation could be that increased surface coverage of hydrocarbons effectively inhibits the NO adsorption and thus results in decreased reduction activity in time. Interestingly, Klingstedt et al. [9] did not report coking as a problem in a real vehicle test, where the Ag/Al_2O_3 catalyst was tested for HC-SCR in combination with a highly optimized modern diesel engine. In addition, the decreased low temperature reduction activity when real diesel fuel is used can be connected to the high aromatic content. According to Ref. [40], reactivity (oxidation activity) of aromatic compounds over silver catalyst is very poor leading to high surface coverage at low temperatures.

A possible explanation for the decreased NO reduction activity at temperatures 300 and 400 °C and high $C_{16}H_{34}$ concentrations (Fig. 7) could be connected to the inhibition of nitrogen oxide adsorption on the surface. At lower temperatures, i.e. clearly below 300 °C, the decreased SCR activity could also be connected to the high boiling point of hexadecane (287 °C). Furthermore, it cannot be totally excluded that at temperatures below 300 °C part of hexadecane might even condense on the surface meaning that oxidation of the hydrocarbon, widely agreed as a key step in the HC-SCR, and the SCR reaction would require diffusion of the gases (O_2 and NO) through a liquid film. This assumption is also supported by the results demonstrated in Fig. 9 and in Table 1. Fig. 9 shows very low oxidation rates of hexadecane in the temperature range 250–350 °C resulting in reaction orders close to

Table 2
Acidic properties of the support and the silver catalyst.

	Brønsted acid sites ($\mu\text{mol/g}$)			Lewis acid sites ($\mu\text{mol/g}$)		
	250 °C	350 °C	450 °C	250 °C	350 °C	450 °C
Al_2O_3	–	–	–	72	30	6
Ag/Al_2O_3	–	–	–	99	25	4

0 for $C_{16}H_{34}$ oxidation with respect to $C_{16}H_{34}$. However, the high boiling point alone cannot explain the reduced reduction activity over the catalysts. In Ref. [40] decreased NO to N_2 conversion was demonstrated using cyclic (methylcyclohexane) or aromatic (toluene) compounds. These compounds have lower boiling points than for instance octane, which resulted in much higher NO reduction over a similar silver catalyst. Thus, the conclusion made above that the size of the hexadecane is the reason for NO adsorption inhibition when the concentration exceeds a certain, temperature dependent, value is more feasible.

Moreover, the effect of the deposition of carbonaceous species on the silver on alumina catalyst at low temperature is a very important matter and surely affects the reduction activity over time. Thus, a detailed study of this effect is under investigation. Nevertheless, even if the activity diminishes in the time-on-stream experiment (Fig. 10) before reaching stable values at 250 °C, it does not affect the results presented in this paper, as the initial activity was used in the kinetic calculations.

3.4. Varying O_2 concentration

The effect of oxygen concentration on the NO to N_2 reduction and $C_{16}H_{34}$ to CO + CO_2 oxidation rates is shown in Figs. 11 and 12. As it can be seen, both the reduction and oxidation rates increase sharply along with increasing oxygen concentration at 400 °C indicating that oxygen is strongly involved in the SCR reaction. At higher temperatures, the reduction rate approaches zero order at oxygen concentration 4.5–6 vol.% and starts to decrease thereafter sharply manifesting the inhibiting effect of oxygen on the SCR route at high temperatures (Fig. 11). Comparing the effect of oxygen on the NO reduction rate and hexadecane oxidation rate at 550 °C it can be concluded that at oxygen concentration 6–9 vol.% it is clearly the route 1 (total oxidation) which dominates, as expected. Moreover, the main increase in both rates takes place between 300 and 400 °C, i.e. at the temperature where the activity exceeds the light off temperature over the catalysts (Fig. 1). Thus, it can be concluded that the activation of NO and hexadecane with oxygen is a key step in the SCR reaction mechanism. In addition, since the oxidation of hydrocarbon depends on the oxygen concentration in a similar way as the NO reduction does, most probably these routes share a common step.

In the work of Shimizu et al. [29] the effect of oxygen concentration for C_3H_8 -SCR is described. As follows, the effect with shorter paraffins is clearly twofold compared to hexadecane-SCR at 400 °C, where a linear dependence between O_2 , NO reduction and $C_{16}H_{34}$ oxidation was found. In C_3 -SCR there is almost no response to the oxidation or reduction at oxygen concentrations between

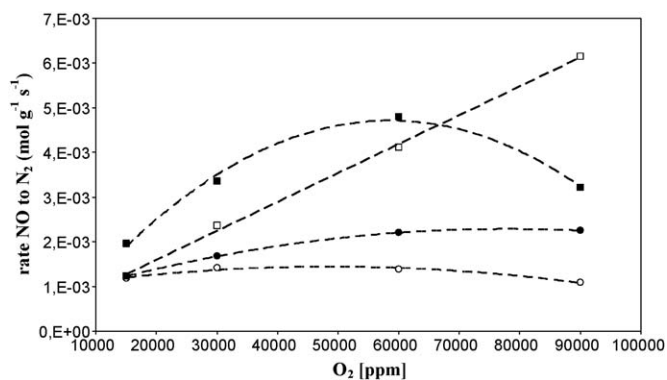


Fig. 11. Effect of O_2 concentration on NO to N_2 reduction rate over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 400 °C (□) and 550 °C (■). Gas flow: 1.5, 3, 6 or 9 vol.% O_2 , 500 ppm NO, 188 ppm $C_{16}H_{34}$, 12 vol.% H_2O and He as balance. GHSV = 120,000 h^{-1} .

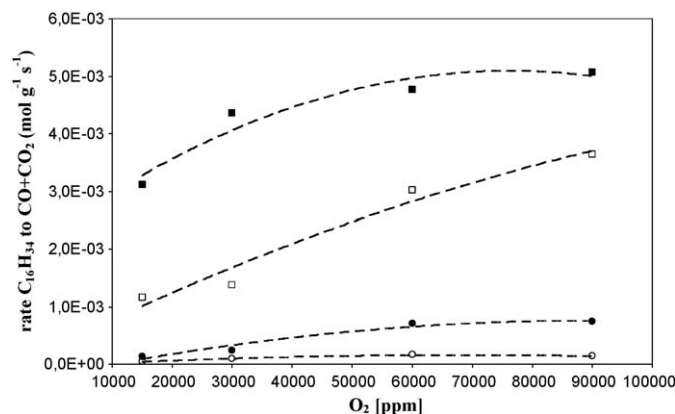


Fig. 12. Effect of O_2 concentration on $C_{16}H_{34}$ to CO + CO_2 oxidation rate over a 1.91 wt.% Ag/alumina catalyst at 250 °C (○), 300 °C (●), 400 °C (□) and 550 °C (■). Gas flow: 1.5, 3, 6 or 9 vol.% O_2 , 500 ppm NO, 188 ppm $C_{16}H_{34}$, 12 vol.% H_2O and He as balance. GHSV = 120,000 h^{-1} .

1.5 and 3 vol.%, whereas in C_{16} -SCR both rates increase linearly clearly indicating different kind of activation of both compounds in propane-SCR compared to hexadecane-SCR. Thus it is clear that the rate of kinetically important steps in HC-SCR depends on the size (C_3 vs. C_{16}) or the chemical nature (cyclic vs. acyclic) of the reducing agent.

3.5. Mechanistic aspects

As mentioned in Section 1, silver supported on alumina is considered as the most promising catalyst for HC-SCR at the moment. The main drawback in the HC-SCR application, however, is that the reaction mechanism, even if it is widely reviewed, is not yet fully understood [6–8,15,17,18,21,22]. This is obviously a serious drawback as the optimization of the catalyst or preparation of more active catalysts is difficult due to the limited amount of knowledge available. In addition, further complexity to understand the system is brought by the fact that the NO reduction over the silver catalyst is strongly connected to the chain length, geometry and nature (functional group) of the hydrocarbon [11,12,41]. Thus, it is possible or even very likely that there are different reaction routes in the mechanism depending whether, for example, aromatic compounds, olefins and paraffins or derivatives of these are used as reducing agents. Even though, at the same time additional information about the reaction intermediates can be gained by using various reducing agents in the experimental work.

Several proposals to describe the mechanism in HC-SCR over the silver catalyst have been made. It is generally considered that the first step in the NO reduction involves the activation of the reducing agent to partially oxidized hydrocarbon species and formation of strongly bound nitrites and nitrates [7]. The adsorbed NO_x species are supposed to react then further with the oxygenates from hydrocarbon yielding organo-nitrogen species, which are transformed to highly reactive intermediates like isocyanates, nitriles, amines and oximes. In the following step of the mechanism these active intermediates are proposed to react directly with NO or NO_2 and/or R-ONO, finally leading to formation of N_2 [7,17]. In addition, understanding the nature of the active sites, which currently is under debate, will enhance the future catalyst development.

Kinetic analysis could be involved in elucidation of complex reaction mechanisms. Carefully produced kinetic data provides valuable information about the reaction mechanism in terms of reaction orders and rate constants, which is, as very well known, essential for optimization of the reactor system for catalytic processes. Unfortunately in the case of Ag/ Al_2O_3 such data is highly

specific for the reducing agent used in the study, meaning that the reaction orders can greatly vary between different hydrocarbons. Thus, creating a kinetic model based on one reducing agent is most likely not suitable to give a satisfactory fit for applications using commercial diesel, which is a mixture of numerous different hydrocarbons and varies greatly between different manufacturers and batches.

In the case of HC-SCR over Ag/Al₂O₃ the reaction mechanism is not fully revealed, even if the adsorbing species and elementary steps are assumed leading to kinetic equations consistent with experimental data [26,42]. In heterogeneous catalysis modelling of adsorption and kinetics is essentially based on the concept of ideal adsorbed layers, following the concepts developed by Langmuir [43]. However, the effect of the shape and size of the metal cluster on the catalyst activity is far from trivial [44]. In the case of the silver catalyst used for lean NO_x reduction, the state of silver and, especially, the size of the active site has been a matter of numerous publications [22,45–52]. Recently, Breen et al. [49] used *in situ* EXAFS to study the size of the silver site and showed that in octane-SCR small clusters of Ag_n^{δ+} are present with average size of three (3) silver atoms. On the other hand, using *ex situ* characterization average silver particle sizes around 5 nm have been reported [53]. Guo et al. [54] showed that after exposing the alumina supported silver catalyst to oxygen, Ag cluster are oxidized and spread over the alumina surface, resulting in smaller particles. This supports the conclusion that small silver clusters exist on the Ag/Al₂O₃ catalyst as suggested in [47–49,52].

If the active site is really such a small cluster of approximately three silver atoms, then it means that the adsorption of the reactants (NO, O₂ and HC) plays a crucial role and special attention should be paid on, how many reactant molecules can adsorb on one active cluster at a time. This is an important issue regarding the catalyst activity, which is rarely discussed in the papers dealing with the Ag/Al₂O₃ catalyst for HC-SCR.

From the results presented in Fig. 7, it can be seen that at 400 °C the NO to N₂ reduction rate goes via a maximum and starts strongly to decrease along with the increasing hexadecane concentration (Fig. 7). At the same time, the hydrocarbon oxidation continues to increase along with the increasing concentration (Fig. 9). It should be noted that at this temperature the conditions are well above the boiling point of hexadecane and the oxygen concentration is kept constant. Such results are conventionally explained with competitive adsorption between hexadecane and nitrogen oxide but not between hexadecane and oxygen. Thus, it can be interpreted that oxygen is available on the active site/cluster all the time.

In the reaction mechanism one or several different adsorption sites can be involved. As shown in Fig. 9, the oxidation of hexadecane takes place on the surface independently of its partial pressure. If oxygen now adsorbs on silver cluster directly, it means that after oxygen adsorption a substantial part of the active cluster, consisting of approximately 3 silver atoms, will be occupied by it if assuming O₂/Ag stoichiometry of 0.5. The other alternative would be oxygen adsorption on alumina, followed by diffusion and migration to the silver cluster. Mao et al. [55] have studied oxygen adsorption on silver (0.71 and 0.83 wt.%) supported on α-alumina. In their study it was suggested that oxygen is rather directly adsorbed on the silver than on the support. Ayame et al. [56] investigated kinetics of oxygen adsorption on Ag/Al₂O₃ during the course of ethylene partial oxidation. In their work, a model where consecutive two-step dissociative oxygen adsorption took place had the best fit to the kinetic data [56]. However, this work was done over a silver alumina catalyst having a considerably higher metal loading than the silver catalyst used for HC-SCR.

Based on the current knowledge about oxygen adsorption on silver, it is reasonable to assume that it is dissociatively adsorbed

on the silver. This leads to a hypothesis where the availability of the rest of the small cluster for NO and HC adsorption depends, not only on their local concentration, but also on the size and shape of the hydrocarbon, which strongly affect on the reduction activity over the catalyst [11,12,41]. For example, Houel et al. [37] proposed that the low temperature deactivation of the Ag/Al₂O₃ catalysts would take place because of coke formation on the active surface. However, they were using commercial diesel (US06) fuel, which includes a considerable share of aromatic compounds (24%). In Ref. [40] it was shown that both the NO reduction activity and hydrocarbon oxidation activity over the Ag/Al₂O₃ catalysts was considerably worse when aromatic or cyclic hydrocarbons were used as reducing agents compared to, for instance, octane. If the hypothesis that the active site is a small cluster is valid, then the adsorption of, for instance, aromatic compounds in a flat mode made the cluster of three silver atoms unavailable for NO adsorption close enough to oxygen and the reducing agent, thus making the catalyst inactive for SCR reaction. Inactivation caused by such reason can be overcome at higher temperatures, where the aromatic compounds are successfully oxidized, and the original activity is regained, as reported in [37]. Of the different aromatics in diesel (mono-, di-, tri- and polyaromatics) benzene, for instance, is the most favorable adsorbed on platinum (111) cluster consisting of four platinum atoms [57] and on silver (111) cluster having the exact dimensions of the proposed size for the active silver cluster for HC-SCR, e.g. 3 atoms [58]. However, theoretical calculations predicting the adsorption of one molecule on an ideal surface not taking the effect of support into account might not give a reliable picture of the surface phenomena on a supported heterogeneous catalyst, on which several molecules adsorb competitively at the same time.

The main drawback in the current level of knowledge about the HC-SCR over the Ag/Al₂O₃ is the substantial degree of speculation regarding the mechanism and kinetics. The reports proposing small silver clusters (around 3 atoms) on the surface provide only the average distance between the silver atoms. It remains unclear what is the distance between these clusters, are they isolated or not and what is the composition of rest of the surface. Such information is crucial considering that the size (chain length, geometry, functional groups) of the reducing agent, which defines the activity over Ag/Al₂O₃, can be several times larger than the cluster size. HRTEM pictures clearly manifest [53] that there are agglomerations of silver on the support, consisting of silver particles with broad size variations and also large areas consisting of only the alumina. However, as reported in [54] silver clusters are oxidized under exposure of oxygen, resulting in small silver particles indicating rather a global even distribution of silver on those areas where silver is present.

As the bare support provides large surface area as well, then a reasonable explanation is that besides HC-SCR on a small active cluster per se, which size greatly limits its availability for reactant adsorption, the support is also involved. Thus, the area around the active silver site is of high importance as it provides the adsorption and storage possibility for the reducing agent and NO_x species. Moreover, as very well known, HC-SCR is a very support specific reaction, which cannot only be explained by mesoporous structure or certain acidity level. Under suitable reaction conditions the both reactants can migrate to the active silver site, on which oxygen most presumably adsorbs, followed by the reactions of hydrocarbon and oxygen and oxygen and NO, finally followed by the SCR reaction on the interface of the silver and alumina. However, if the local concentration of the hydrocarbon is too high, then the active metal site will be surrounded or covered by it, resulting in decreasing NO reduction rates. The activity is reported to strongly depend on the nature of the hydrocarbon used [11,12,41], which means chain length, spatial arrangement and presence of

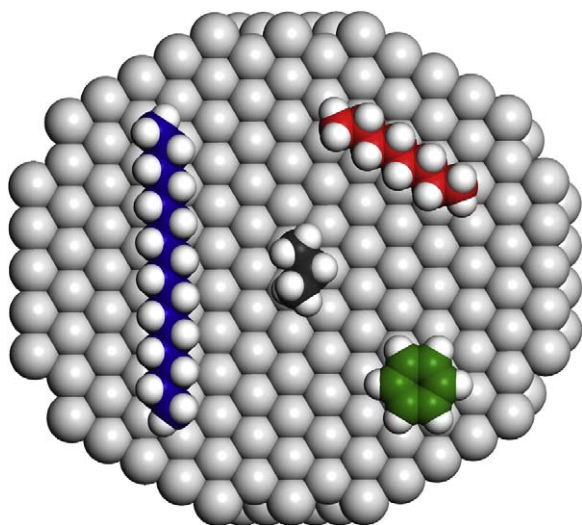


Fig. 13. Scheme of n-hexadecane, n-propane, n-octane and benzene adsorption on a silver cluster having approximately 3 nm diameter.

functional groups. Fig. 13 illustrates this concept for few hydrocarbons, i.e. benzene, propane, n-octane and n-hexadecane. In that figure a silver particle having approximately 3 nm diameter, based on HRTEM images, is presented. Logically, different hydrocarbons occupy different amount of silver atoms on the surface depending on the chain length, spatial arrangement and presence of functional groups. NO, on the other hand, is always present in the system and has no direct size effect, and thus its influence is directly linked to its partial pressure. This indicates that no strictly defined active cluster size can be valid for HC-SCR over Ag/Al₂O₃ catalyst. Different characterization methods, e.g. EXAFS and HRTEM, results in different cluster size. However, it should be kept in mind that the high level of simulation involved in the interpretation of the results from EXAFS studies makes the conclusions rather unsecure. Thus, the results based on electron microscopy could be taken with higher confidence.

4. Conclusions

The kinetic behaviour of NO reduction with hexadecane under lean conditions was investigated over a 1.91 wt.% Ag/alumina catalyst in the temperature range 250–550 °C. Not only the reduction activity but also the kinetic behaviour of C₁₆H₃₄-SCR was found to be different from that of n-octane-SCR. The main difference between the two compounds was that the activity over the catalyst in n-C₁₆H₃₄-SCR was found to predominantly depend on the hydrocarbon concentration both at low and high temperatures. In n-C₁₆H₃₄-SCR the NO reduction activity was increased by decreasing the hydrocarbon concentration in the temperature range 200–325 and, vice versa, the reduction activity increased by increasing the reductant concentration in the temperature range 450–600 °C. Based on the kinetic results the surface coverage of NO is clearly lower and hydrocarbon coverage is clearly higher in hexadecane-SCR than in octane-SCR resulting in the conclusion that the chain length or the chemical structure of hydrocarbon determines the surface coverage of the reacting species on the surface.

The NO reduction rate was found to increase along with the increasing NO concentration until approaching zero order kinetics. The reaction orders (around 0.5) indicated relatively high surface NO surface coverage but were clearly lower than in octane-SCR. The effect of hexadecane concentration on NO reduction rates was, however, found to be twofold: at 300 and 400 °C, i.e. at the

temperature where the catalyst reaches its maximum activity, the rates pass through a maximum after which increasing hexadecane concentration starts strongly to inhibit the NO reduction. Such behaviour was not detected in C₈H₁₈-SCR at comparable hydrocarbon concentrations. These observations highlight the effect of hydrocarbon chain length on the HC-SCR over Ag/alumina catalyst as the aromatic or cyclic hydrocarbons manifest the effect of molecule geometry compared to straight chain hydrocarbons.

The kinetic observations also manifested the importance of oxygen activation of both NO and hexadecane for an effective HC-SCR. Depending on the temperature 6 or 9 vol.% oxygen resulted in the highest NO to N₂ reduction activity over the catalysts.

It is proposed that small clusters alone cannot be the active sites for HC-SCR over Ag/Al₂O₃ but the important requirement for high activity over the catalyst is the local concentrations of hydrocarbon and NO on the interface of silver and the support. Moreover, the reduction activity is not only a function of the hydrocarbon concentration, but also of its chain length, spatial arrangement and presence of functional groups. Therefore, the optimum size of the active silver cluster should be adjusted taking into account these properties of the reducing agent.

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